ON THE CHEMICAL NATURE OF THE
BENZENE INSOLUBLE COMPONENTS OF SOLVENT REFINED COALS

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INTRODUCTION

The present emphasis on the conversion of coal to substitute pet-
roleum fuels has led to several alternative processes which are
now being investigated.

Among the many processes being considered is the solvent refining
of coal (SRC) in which coal is treated at an elevated temperature
in the presence of a hydrogen-donor solvent and hydrogen gas to
lower the sulfur content of the coal, remove the mineral matter,
and convert it into a low melting solid which can be solubilized
in simple organic solvents. The work reported here is concerned
with developing a fundamental understanding of the chemistry of
this process.

Little is known at present as to the exact mechanisms by which the
coal is transformed into soluble form, the detailed chemical struc-
ture of the soluble product, or even of the parent coal. It is
known that many coals are easily solubilized and others are more
difficult (1).

A common means of fractionation and characterization of SRC pro-
ducts is through solvent extraction. The major classifications
referred to include oils (hexane soluble compounds), asphaltenes
(benzene soluble-hexane insoluble compounds), and less soluble ma-
terials (pyridine soluble-benzene insoluble compounds). Of these,
the asphaltenes and pyridine soluble-benzene insoluble materials
are believed to be responsible for high viscosity, solvent incom-
patibility, and processing difficulties.

Often the extent of coal conversion is measured in terms of the
solubility characteristics of the product, and mechanisms for coal
conversion involving such classifications have been proposed (2-4).
The reported mechanisms conclude that asphaltenes are a necessary
product of coal conversion and that they are the primary precur-
sors of oils (2-4).

Some recent work has been reported (5-8) on further fractionation
and characterization of SRC products. However, the major emphasis
has primarily concerned oils and asphaltenes. We will show that
at low conversions of coal, the concentration of benzene insoluble
compounds can amount to 70-80% of the total SRC, and therefore these
are of great importance in understanding the mechanisms of coal con-
version.

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EXPERIMENTAL

The molecular weights and elemental analyses of various coal pro-
ducts were determined by Galbraith Laboratories, Inc., Knoxville,
Tennessee, and Spang Microanalytical Laboratory, Ann Arbor,
Michigan.

The IR spectra were measured on a Perkin-Elmer 237B grating infra-
red spectrophotometer. The NMR spectra were measured on a Varian
A-60 spectrophotometer for H-NMR; ^{13}C NMR were determined using a
Varian XL-100 spectrophotometer by G. Mateescu of Case Western
Reserve University, a Varian CFT-20 spectrophotometer by G. Gray
at Varian, and a JEOL FX-60 spectrophotometer by R. H. Obenhauf of
JEOL.

A duPont 950 thermogravimetric analyzer was used to determine the
weight vs. temperature profile of coals and coal products. Polaro-
graphic reductions were performed by F. Rogers of the Department
of Aerospace and Mechanics, Princeton University. The apparatus
used was the Princeton Applied Research (PAR) Model 174 Polarographic
Analyzer, using a dropping mercury electrode in the differential
pulse mode.

All extractions were performed using a Soxhlet extraction apparatus
with controlled N_2 or Argon atmosphere. Paper thimbles were used
and extractions were carried to exhaustion (generally ~17 hr.).

The conversion apparatus has been described in detail elsewhere
(10,11). Briefly, it consists of a stirred batch autoclave in
which solvent is heated to reaction temperature. A 1:1 coal: sol-
vent slurry is then injected. To quench, water under pressure is
forced through a cooling coil in direct contact with the vessel con-
tents. Conversion times as short as 0.5 min. at reaction tempera-
ture are routinely achieved.

The synthetic solvent has also been described in detail elsewhere
(10,11). It is ~2% 4-picoline, 17% p-cresol, 43% tetralin, and 38%
2-methyl-tetralin.

RESULTS AND DISCUSSION

In order to obtain a fundamental understanding of the chemical nature
of coal and the organic mechanisms involved in its conversion to
soluble form, we felt it necessary to develop a method of chemical
fractionation of the whole SRC.

The use of extraction (to separate the pentane soluble and benzene
soluble fractions) has a very limited utility from a fundamental
chemical standpoint. The solubility of different substances is not
only a function of the molecular weight, carbon-hydrogen skeleton,
and chemical functionality, but also depends on interactions with
other soluble species which can act as cosolvents. Therefore, the
same compound can appear as "oil" or as "asphaltene," depending upon
the presense or absence of other species in coal liquids. Even in

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very carefully performed extractions or precipitations, some products will often be distributed between extract and residue because of limited solubility.

Accordingly, a liquid chromatographic procedure for chemical fractionation of SRC was developed. This method, which we refer to as SESC, uses silica as the stationary phase, and is described elsewhere (9,10). To the best of our present understanding, the elution solvents, the resultant chemical classes obtained with this method, and the relationships between the fractionation solubility classifications, are shown in Figure 1. As can be seen, asphaltenes are primarily monofunctional compounds, and oils contain appreciable amounts of non-hydrocarbons (primarily ethers and thioethers).

The benzene insoluble materials, although less completely defined, are clearly distinguished from asphaltenes and oils by a higher degree of functionality. Our preliminary evidence indicates that this higher functionality is primarily in the form of more -OH groups per molecule, as will be discussed later. Accordingly, we propose the name asphaltols for this class of compounds, and will refer to them as such in this report.

It is commonly believed that in order to convert coal eventually to oils, a sequence of reactions must occur with increasing heteratom removal at each stage of the sequence. A generalized scheme, including definitions of terms used in this report and approximate heteroatom content at various stages of conversion, is outlined below:

Coal	→	Insoluble Solids	→	Pyridine Soluble Compounds	→	Benzene Soluble Compounds	→	Hexane Soluble Compounds
Terms		Residues & Char		Asphaltols		Asphaltenes		Oils
Heteroatom Content		>10% res. 1-10% char		5-10%		~2%		1% or less

If one assumes a sequential reaction of coal → asphaltene → oil, then a kinetic description of the progress of the reaction can be obtained by plotting the composition of the soluble product vs. the yield of total soluble product. Earlier reports (2-4) indicated that asphaltenes were primary products from coal, and indeed if the reported data are plotted in this way, this assumption appears to be valid (see Figure 2). These data, however, were obtained in the absence of any hydrogen donor solvent.

Since asphaltols were not accounted for in the reported kinetic studies (2-4), we conducted for comparison a series of coal conversions using West Kentucky 9,14 coal using procedures previously described (10,11). The results shown below indicate that at low coal conversion levels, asphaltols are the predominant products.

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Run #	Extract	9	10	7	12
Reaction Time (min.)	0	1.3	0.5	40	417
% O in SRC	9.47	7.25	6.68	5.15	2.93
wt. % Hexane Soluble (oils)	8.3	5.1	7.1	10.3	32.1
wt. % Benzene Soluble (asphaltenes)	11.7	8.6	13.5	18.8	28.4
wt. % Benzene Insoluble (asphaltols)	80.0	86.3	79.3	70.8	39.5
wt. % SRC Yield	28.0	76.1	46.8	73.2	61.1
wt. % Conversion to soluble form	28.0	78.2	50.0	93.0	96.1

When these data are plotted in the above described manner (Figure 3), it can be seen that the commonly accepted sequential description for the conversion of coal to oils through asphaltenes appears not to be operative when hydrogen donor solvents are present. A more correct interpretation of the conversions involved appears to be that asphaltols are predominant, primary products (some asphaltenes and oils are formed in parallel from the coal), and the asphaltols are then converted in a parallel fashion to asphaltenes and oils, with a small preference for the formation of oils.

Early in the conversion process (<5 min.) we find, by gel permeation chromatography, that the product in solution may be up to 40% high molecular weight (>2,000 MW) or very strongly associated molecules. These high molecular weight species would be classified as asphaltols and are found in fractions 9 and 10 of our fractionation procedure (SESC). The relative concentration of this material then rapidly declines, producing material in the 300-900 MW range. In coal extractions, this material is in the THF insoluble, pyridine soluble portions. Typical results for the conversion of Wyodak coal at 800°F in H_2 and our synthetic solvent are shown below:

	Wt. % of Original Coal		
	Low	High	
	Molecular	Molecular	
Time, min.	Weight	Weight	Total
1.20	16.86	10.97	27.80
3.60	15.41	6.13	21.53
6.00	44.32	8.48	52.80
19.50	44.99	6.70	51.69
38.00	65.77	6.87	72.64
74.00	66.45	4.79	71.24
137.50	70.54	4.03	74.57

Because of the predominance of asphaltols during the initial stages of coal conversion, we have begun detailed chemical characterization of these materials as well as kinetic and mechanistic studies on their conversion under typical solvent refining conditions.

Isolation of the materials was accomplished by preparative SESC or selective extractions. Three SRC's produced in pilot plants were studied; Illinois #6 and West Kentucky 9,14 SRC's, produced by the pilot plant operated by Catalytic, Inc., for Southern Services, Inc. at Wilsonville, Alabama, and Wyodak SRC, produced by Hydrocarbon Research, Inc. in Trenton, New Jersey. The quantity of the fractions isolated, their corresponding elemental analyses and molecular weights are shown in Figures 1 and 2, for West Kentucky and Wyodak, respectively. The emperical formulae for various fractions are also shown.

We have developed semiquantitative correlations between the SESC fractionation and solubility classification as shown in the tables. An interesting consequence is the fact that the partitioning of a given SESC fraction into either benzene soluble or benzene insoluble material is a function of the original coal as well as the degree of conversion. For example, with West Kentucky SRC, oils constitute SESC fractions 1, 2 and 1/2 of fraction 3. Asphaltenes constitute 1/2 of fraction 3, fraction 4, and 1/2 of fraction 5. With Wyodak SRC, fraction 5 is completely benzene insoluble.

In comparing the composition of the various fractions, it can be seen that West Kentucky SRC fractions have higher molecular weights for asphaltols than for oils or asphaltenes; however, with Wyodak SRC the molecular weights are approximately the same. With both SRC's the asphaltols have >3 oxygen atoms per molecule, indicating a high degree of functionality. An increasing -OH content with increasing fraction number can be seen by infrared spectroscopy as shown in Figure 4.

To gain understanding as to the type of molecules that can be found in the various asphaltol fractions, we have conducted SESC analyses of a number of model compounds, and have tabulated below in which fraction they appeared:

Fraction 5 - Basic Nitrogen and Di and Tri Functional Oxygen

Chrysin
Julolidine
N,N'-di-(2-naphthyl)-p-phenylene diamine
Naphthoflavone
Veratrine (mix of alkaloids)*
Anthrarobin

Fraction 6 - Polyfunctional

8-hydroxyquinoline
Rutin
nicotinamide

Fraction 7 - Polyfunctional

(No models could be found)

Fraction 8 - Polyfunctional

6,13 dihydrodibenzophenazine

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Fraction 9 - Polyfunctional

        Veratrine (mix of alkaloids)*
        Phenolphthalein

   *   Alkaloids were found in both fractions 5 and 9.

All model compounds occurring in these fractions have multiple
functionality.

The aromatic content of the various SESC fractions are shown in
Table 3. A general trend appears to be that the asphaltols have
less aromatic hydrogen and aromatic carbon than the less functional
materials, and more closely resemble the composition of the parent
coal (12).

It should be noted also that polarographic analysis of asphaltols
indicates that the number of condensed aromatic rings (more than
2 rings) is quite small.

A distinguishing characteristic of asphaltols as compared to as-
phaltenes or oils is their behavior on pyrolysis in inert atmos-
pheres. In Figure 5 it can be seen that asphaltols yield up to 80%
char on pyrolysis in inert atmosphere. This char formation occurs
in the temperature regime of coal liquefaction and could well con-
tribute to high coke make during SRC processing. Attempted dupli-
cation of this behavior with model compounds indicated that increas-
ing char formation tendency paralleled increasing -OH content; how-
ever, no model compounds could be found that could produce char at
the magnitude found for asphaltols.

Based on the above information, a formal average structure for West
Kentucky asphaltol (SESC 8) can be constructed as shown in Figure
6. Structures of this type can easily aromatize, with elimination
of H or through skeletal rearrangement. If one attempts a similar
treatment of the data for Wyodak asphaltols, a much more condensed
polycyclic aliphatic structure must be proposed. The structure of
all fractions of SRC change with increased severity of coal conver-
sion. The products generally increase in both total aromatic and
highly condensed aromatic ring contents; H/C ratio and total hydrogen
contents decrease (11).

To gain insight into the chemistry and reactivity of these highly
functional materials, several fractions or concentrates were con-
verted under typical SRC processing conditions, and the products
analyzed. The results are presented in Table 4. It can be seen
that asphaltols, relative to asphaltenes, tend to produce less oil
and more pyridine insolubles (char) and consume less hydrogen, but
an important observation is that both asphaltenes and asphaltols
produce all classes of products. Hydrogen consumption appears to
correlate with the production of oils and solvent-range material,
not gases. These general observations have been confirmed by addi-
tional runs, not shown here.

In conclusion, we would like to reemphasize the importance of asphal-
tols in the initial stages of coal liquefaction. Their propensity

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toward char formation at temperatures comparable to liquefaction temperatures, their high degree of functionality, and the fact that they are the predominant, primary products of coal, indicate that much valuable information which could relate to criticalities in the SRC process could be obtained by a more thorough understanding of their chemistry and structure.

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[12]   Data on the aromatic content of coals will be published in the near future.

Figure 1

CHEMICAL FRACTIONATION OF SRC VIA MOBIL'S SESC PROCEDURE

Classical Description	Fraction	Elution Solvent	Major Compounds
Oils (1-3)	1	Hexane	Saturates
	2	Hexane/15% Benzene	Aromatics
Asphaltenes (3-5)	3	Chloroform	Polar aromatics; nonbasic N, O, S-heterocyclics
	4	Chloroform/10% Et$_2$O	Simple phenols
	5	Et$_2$O/3% EtOH	Basic nitrogen heterocyclics, di and triphenols
Multifunctional Cpds. (5 thru 9)	6	MeOH	Highly-functional molecules (>10 wt. % heteroatoms)
	7	CHCl$_3$/3% EtOH	Polyphenols
	8	THF	Increasing O content and increasing basicity of nitrogen
	9	Pyridine	
	10		Non-eluted, unknown materials

SELECTIVITY VS. CONVERSION

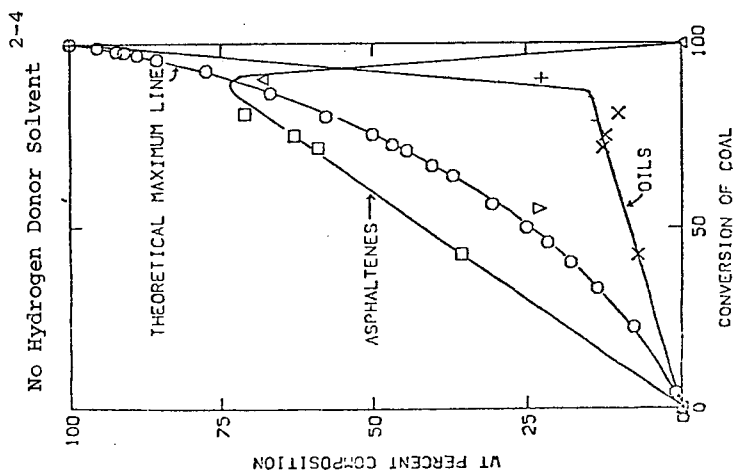Hydrogen Donor Solvent

Figure 3

No Hydrogen Donor Solvent 2-4

Figure 2

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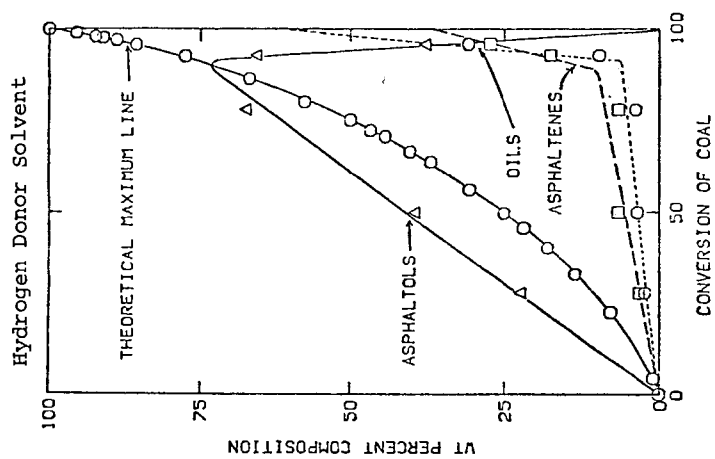
Figure 4

INFRARED SPECTRAL ANALYSES OF SELECTED WEST KENTUCKY SRC FRACTIONS

Figure 5

TGA of West Kentucky Coal and SRC Fractions

25°C — 5°/min. → 800°C
Helium Atmosphere (150 cc/min.)

(ASPHALTOLS)
(Benzene Insoluble) SRC

COAL

(ASPHALTENES AND OILS)
(Benzene soluble) SRC

Wt. % Residue

Temp, °C

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Formal Average Structure for West Kentucky Asphaltol

(SESC 8)

$C_{61}H_{46}N_2O_4$

900 mol. wt.

73% Aromatic C

60% Aromatic H

Figure 6

Table 1

Percentage of the Fractions and Elemental Analyses of West Kentucky SRC Fractions Obtained by Preparative SESC
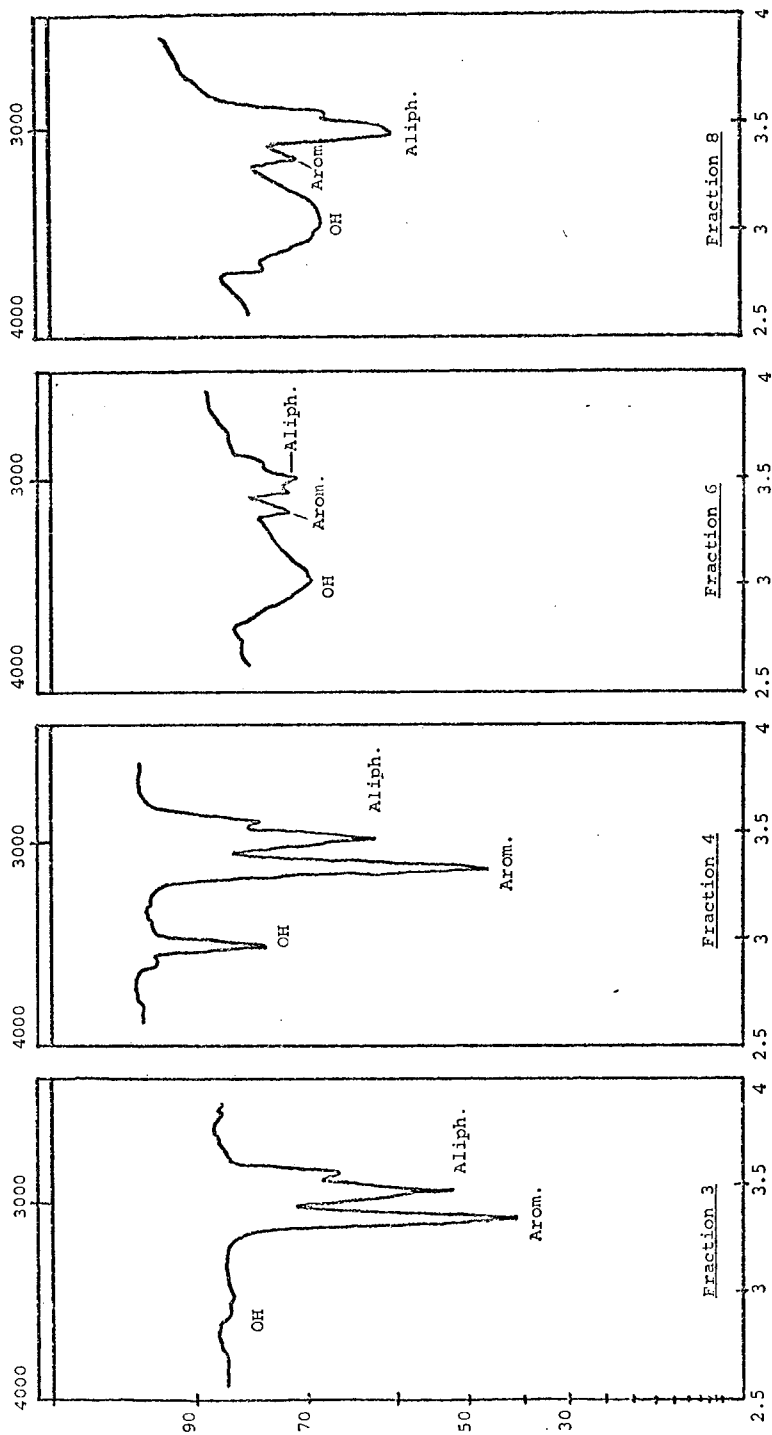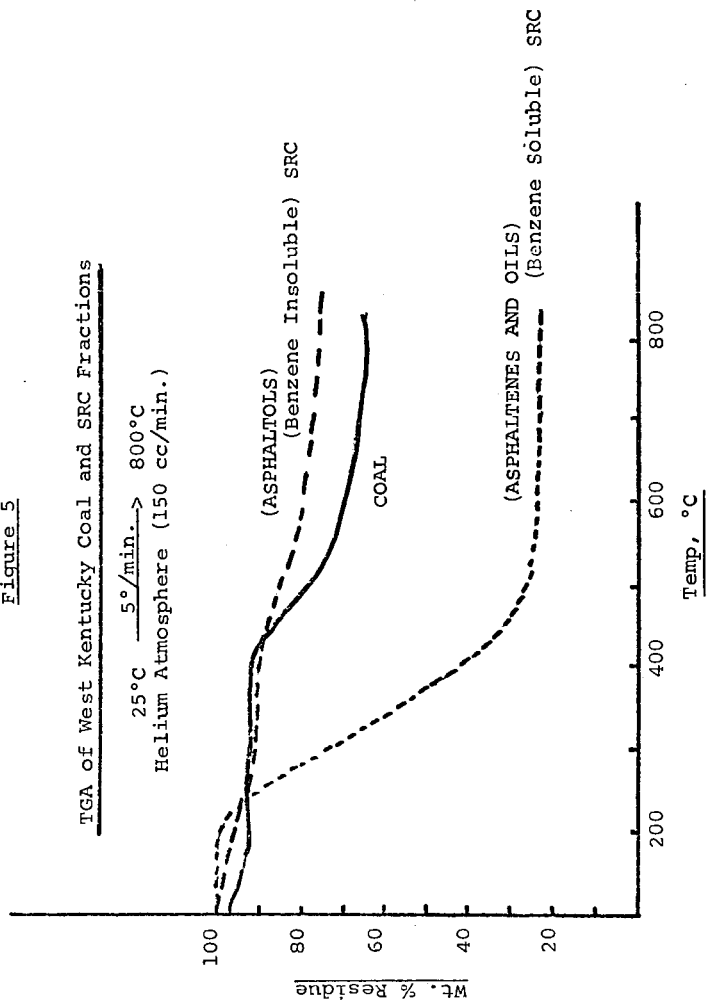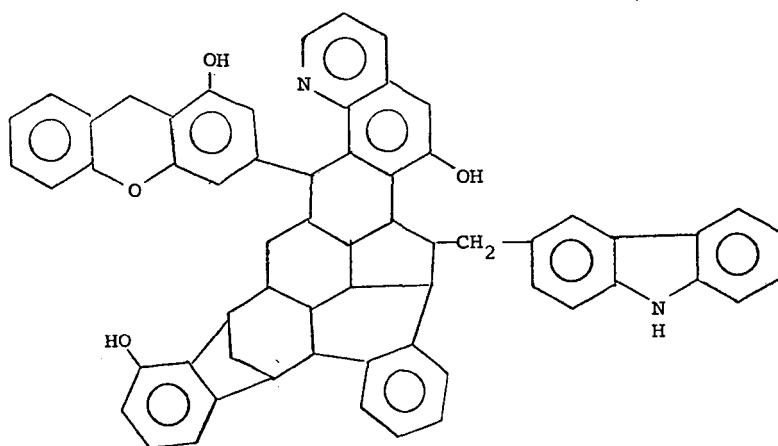
Fraction	% in SRC	Elemental Analyses					MW	Emperical Formulae
		% C	% H	% O	% N	% S		
SRC	100	87.60	4.80	3.4	2.0	.80		
1	0.4							
2	15							
3	30	91.8	5.38	1.06	0.85	0.8	325	$C_{24}H_{16}O$, $C_{24}H_{17}N$
4	10.2	86.3	5.33	5.2	2.32	0.8		$C_{22}H_{17}NO$
5	10.1	87.6^a	5.35^a	$\sim 2^b$	3.81	1.36	~400	$C_{30}H_{25}NO_2$
6	4.1	68.58^a	4.82^a	$20.05^{a,b}$	4.77^a	1.36		
7	6.4	83.6	5.1	7.78	2.57	0.94	$(600)^c$	$C_{41}H_{30}NO_3$
8	10.2	81.91	5.14	7.7	2.73	1.7	~900	$C_{61}H_{46}N_2O_4$
9	8.5	83.7^a	4.5^a	$8.3^{a,b}$	2.51^a	0.9^a	$(900)^c$	$C_{63}H_{41}N_1O_5$

Oils (1-3)

Asphaltenes (3-5)

Asphaltols (5-9)

(10 non-eluted) ca. 5

a) results from a different preparative run
b) oxygen by difference
c) estimated molecular weight

Table 2

Percentage of the Fractions and Elemental Analyses of Wyodak SRC Fractions Obtained by Preparative SESC

	Fraction	% in SRC	Elemental Analyses					MW	Emperical Formulae
			% C	% H	% O	% N	% S		
Oils (1-3)	1	0.5	92.14	6.40					
	2	7.6	89.7	6.15	~3	1.1		660	$C_{49}H_{41}NO$
	3	20.8	85.2	6.07	6.3	2.0		630	$C_{45}H_{38}NO_2$
Asphaltenes (3-5)	4	20.0	79.5	6.57	11.0	1.8	.76	580	$C_{40}H_{38}NO_4$
	5	10.7	74.3	6.01	11.7	2.6	.65	(600)[a]	$C_{37}H_{36}NO_4$
Asphaltols (5-8)	6	4.4	84.3	5.57	6.1	1.9			
	7	4.7	81.6	5.84	9.95	1.6		740	$C_{50}H_{43}NO_5$
	8	16.3							

a) Estimated molecular weight

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Table 3

NMR Analysis of SRC Fractions

Parent Coal	SESC Fraction	Aromatic Hydrogen (9-6 ppm)	Aromatic Carbon
West Kentucky 9,14	2	82	83
West Kentucky 9,14	3	81	74
West Kentucky 9,14	4	63	65
West Kentucky 9,14	5	49	73
West Kentucky 9,14	8	60	
Wyodak	2	56	80
Wyodak	3	48	64
Wyodak	4	47	53
Wyodak	5	47	
Wyodak	6	36	60
Wyodak	8	45	

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Table 4

Conversions of Asphaltenes and Asphaltols at 800°F in H_2 and Synthetic Solvent

Run	13	36		39		51	
Parent Coal	Illinois #6	Wyodak		Wyodak		Wyodak	
Feed Concentrate	Asphaltols	Asphaltenes		Asphaltols		Asphaltols	
Time, mins.	84	111		20		20	
Products (MAF)*							
Gases (C_6^-)	4.9	13.7		25.4		7.6	
Solvent Range	21.1	20.9		2.4		7.6	
SRC	61.1	58.2		62.4		65.3	
Residue	12.7	6.4		9.7		19.5	
SRC* (oils)**	25.6	34.6		7.9		12.6	
(asphaltenes)**	23.0	26.3		36.9		35.6	
(asphaltols)**	51.4	39.2		55.2		53.03	
Wt. % H-Consumption	2.2	4.7		0.6		0.6	
Wt. % H-Consumption (at 20 mins.)	1.4	1.9		0.6		0.6	
Detailed SESC Analyses*	F‡	P‡	F	P	F	P	F	P
Fraction 1	0	5.5	0.2	1.4	0	1.8	0	0
Fraction 2	0	9.9	2.1	27.7	0	3.4	0	8.3
Fraction 3	0	20.5	2.4	10.9	1.2	5.5	4.7	8.6
Fraction 4	0.6	9.4	54.7	16.3	13.7	28.7	20.6	25.8
Fraction 5	1.5	6.7	30.3	9.1	16.1	10.9	12.2	10.9
Fraction 6	3.1	4.6	6.5	22.8	7.5	6.5	6.1	3.6
Fraction 7	6.4	10.3	2.0	5.1	27.3	7.1	17.5	10.2
Fraction 8	15.4	18.4	0.6	1.7	23.3	8.7	16.1	10.4
Fraction 9	73.0	14.8	1.4	5.0	17.7	27.4	20.6	23.4

* Normalized to 100%. **These data represent only the eluted materials.

‡ F = feed; P = product

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